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FATE AND TRANSPORT OF CREOSOTE DNAPL AND DISSOLVED CONSTITUENTS IN ROCK AQUIFER, SWP SITE, CHATTANOOGA, TENNESSEE

Prepared for:

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1.0 INTRODUCTION

This position paper addresses the potential threat to human health and the environment from the transport of coal tar-derived heavy creosote and dissolved creosote constituents in the rock aquifer underlying the Southern Wood Piedmont (SWP) Site in Chattanooga, Tennessee. The location of the site is shown on Figure 1.

During site assessment, organic contaminants associated with past operation of the creosote wood treating plant were detected in soil and rock beneath the site. Both creosote oil and constituents of creosote dissolved in groundwater were found at the site. Creosote is a viscous oil that is heavier than water and belongs to the group of Dense Non-Aqueous Phase Liquids (DNAPLs or "sinkers") which travel in soil and rock mainly due to the force of gravity (i.e., vertically) rather than being transported laterally by ground water. Dissolved creosote constituents, on the other hand, travel with ground water but at lower velocities than ground water due to various natural attenuation processes such as dispersion, diffusion, sorption and degradation.

Southern Wood Piedmont (SWP) has performed extensive investigation and remediation of contaminated soils and ground water at the site since the discovery of contaminants in the early 1980's (see Figures 2, 9 and 14). SWP currently monitors ground-water conditions at the site, intercepts, extracts and subsequently treats contaminated ground water removed from the soil and fractured-rock aquifers.

2.0 GEOLOGY

The SWP site is located within the Valley and Ridge Physiographic Province near the boundary with the Appalachian Plateau Physiographic Province. The Valley and Ridge Province is characterized by northeast-southwest trending elongated valleys and ridges composed of sedimentary rocks: predominantly limestone, shale and sandstone which were formed during the Paleozoic era, 230 to 600 million years ago. Ridges are formed of resistant layers of sandstone while the valleys are underlain by more erodible limestone and shale. The rocks of the Valley and Ridge Province are typically folded into elongated anticlines and synclines which have been subject to faulting and have moderate to steep angles of dip.

The rock units in the site vicinity are shown on a geologic map on Figure 3 (modified from Rodgers, 1953). The bedrock underlying the site belongs to the Lower-to-Middle Chickamauga Supergroup of the Ordovician period (formed 430 to 500 million years ago). Specifically, the bedrock at the site is mapped as the Stones River Group and consists primarily of limestone with interbeds of shales, mudstones, and bentonite. This is determined by correlation between the drilling results and geologic maps (Rodgers, 1953), outcrops described in the literature (Wilson, 1979a) and local geologic knowledge (Dafferner, 1988), and by comparison with drilling core of known lithologies stored by the Tennessee Division of Geology. It is estimated that the Stones River Group ("Chickamauga limestone") is well over 1000 feet thick beneath the western site boundary and about 600 feet thick near Chattanooga Creek. Chickamauga limestone is underlain by the Knox Group (predominantly dolomite) of Cambrian to early Ordovician age (formed about 500 to 600 million years ago). Borings about 100 feet deep along Chattanooga Creek did not encounter the next lower geologic unit, the Knox dolomite.

Over 150 soil and rock borings and 25 test-pit excavations have been performed at the SWP site as part of the overall site assessment (SWP, 1988, 1990). Soils at the site consist primarily of residual material (sandy clay) with man-made fill present within portions of the former main plant area and alluvial deposits of the Chattanooga Creek floodplain. The alluvial deposits consist of clay, silt, sand and gravel. Residual soil at the site is 10 to 40 feet thick (see Figure 4).

3.0 HYDROGEOLOGY

Based on extensive hydrogeologic investigation; including drilling, coring and logging of 56 boreholes, hydraulic testing, monitoring well installation, and consistent measuring of ground-water levels, the rock beneath the site can be generally categorized by two hydraulic conductivity zones. The upper portion of rock (immediately below the residual soil) is more fractured and weathered, has higher permeability for ground-water flow (see Figure 4) and therefore constitutes the rock aquifer at the site. Hydraulic conductivity is typically above $1x10^{-5}$ cm/sec (see Figure 11). Fracture zones within the rock aquifer (i.e., severely fractured and weathered rock with no core recovery logged as "voids" and/or "cavities" during rock coring) were also field tested at the site and yielded values of hydraulic conductivity between $1x10^{-3}$ and $1.6x10^{-4}$ cm/sec (locations C-21A, P-4, P-11, P-12, and U-4A - SWP 1990). Within this upper severely fractured and weathered limestone, where the limestone could be dissolved by circulating ground water (such as along larger fractures) the fractures have most likely collapsed and infilled so that the formation of extensive or connected cavities has not occurred. This "collapse" mechanism is indicated at the site both by the tested hydraulic conductivity (10^{-3} to 10^{-4} cm/sec range) across zones of logged "voids" and by the ability to fill one borehole within a logged "cavity" with a relatively small quantity (about 44 ft^3) of cement grout (abandoned borehole C-22A) adjacent to another borehole with core loss zones in rock logged as cavities (well C-22B).

Beneath the fractured rock is a zone of low hydraulic conductivity rock (less than $1x10^{-5}$ cm/sec). At depths of 60 to 80 feet below the land surface, the hydraulic conductivity of the rock generally drops to less than $1x10^{-7}$ cm/sec indicating the bottom of the rock aquifer (see Figure 11). This value is comparable to that of clay sediments which are commonly considered "confining units" due to their lack of ability to effectively transmit fluids. The absence of significant ground-water circulation in the deeper rock at the site is evidenced by deep monitoring wells (e.g., C-31B, C-29B and L-4E) which repeatedly cannot be sampled due to the lack of water (SWP, 1997). The deeper portion of the Stones River Group underlying the site exhibit low hydraulic conductivity because the formation is made up of thinly bedded limestone interbedded with low permeable shales, mudstones and bentonite (Luther, 1979; Rodgers, 1953; Wilson, 1979a).

Ground-water flow in rock at the site is directed toward the ground-water interceptor trench by its operation (i.e., pumping water from the trench). The portion of the site affected by pumping from this trench has curved equipotential lines and the corresponding flow lines (arrows) show flow direction toward the trench (see Figure 6). The maps on Figure 6 are constructed from data collected in monitoring wells completed in the rock aquifer. The hydraulic heads in the rock aquifer are affected by the trench during both high and low flow conditions as shown by the equipotential lines on Figure 6. The trench was installed by SWP near Chattanooga Creek which was the natural discharge line for the rock aquifer beneath the site before installation of the trench. Figure 7 shows the location of the SWP site on an aerial photograph and its relation to nearby residential and industrial areas. As can be seen, ground-water flow direction is away from residential and industrial areas and toward Chattanooga Creek.

Figure 8 shows the results of a well survey performed by LAW (SWP, 1988 & 1995). The results of the survey show that the existing water supply wells are used for industrial purposes which is generally consistent with other wells in the Chattanooga area (Wilson, 1979b). The majority of the industrial water supply wells in the SWP vicinity are completed in formations other than the Stones River Group (i.e., Lower-to-Middle Chickamauga). The wells that are completed within the Lower-to-Middle Chickamauga formations are located near major geologic features, including the two thrust faults and the boundary between the Stones River Group and the adjacent formations.

Hydrogeologic findings at the site are in agreement with regional knowledge about water-bearing characteristics of the Stones River Group rocks - they are described as yielding moderate amounts of water to wells (Wilson, 1979b). For example, out of 12 wells drilled into the Lower-to-Middle Ordovician in Chattanooga, 4 reported difficulties either with amounts of available water or natural water quality (DeBuchananne and Richardson, 1953). Two wells reported a 160 foot drawdown after 10 and 30 minutes of pumping. One well, drilled 613 feet deep, encountered no appreciable amounts of water below 50 feet. The fact that water wells in the Stones River Group often exhibit unsatisfactory yields and/or excessive drawdowns clearly indicate absence of a significant, interconnected network of water bearing fractures in the deeper rock. Other limestones and dolomites in the region, such as those of the Knox Group, are considered much better aquifers (Wilson, 1979b).

The location of the site with respect to hydrogeologic conditions and the directions of ground-water flow at the site indicate that dissolved contaminants traveling with ground water in the rock do not have any impact on known wells in the site's proximity (see Figure 8).

As part of the "Dye Tracer Study Report, Velsicol Chemical Corporation Facility", Quinlan and Associates, Crawford and Associates, and Law Engineering and Environmental Services (1994 through 1997) performed a very detail inventory of ground water and surface water for the entire section of the Chattanooga Creek from the Tennessee/Georgia state line to the Creek's confluence with the Tennessee River. This study shows that, in the wide area that could potentially be impacted by the SWP site, there are none of the features usually associated with well-developed limestone (karst) aquifers. The study did not find any sinkholes, sinking streams, caves or springs flowing from bedrock conduits (LAW with Crawford and Associates, Inc., 1997). The study area has surface streams, seeps, ponds and swamps, all indicative of a high water table and poor subsurface drainage. Also, similarly to the SWP site conditions, the water table in most of the monitoring wells at the Velsicol site (located upstream from the SWP site) indicate slow drainage in the underlying bedrock. Therefore, the Velsicol study and the data collected at the SWP site, which is situated nearby in very similar geologic conditions, confirm that there is no evidence of karst features or a karstic aquifer in the study area.

4.0 NATURE AND EXTENT OF CONTAMINATION IN ROCK

The rock aquifer underlying the SWP site is found to be contaminated with both free and dissolved-in-groundwater phases of creosote. Creosote is distilled from coal tar, a waste product of coal or oil gasification, and iron and steel production. It consists of various coal tar distillates (primarily the 200°C to 400°C fraction) which are blended to meet American Wood-Preservers' Association product standards. The SWP plant in Chattanooga operated between 1925 and 1988 using only creosote as a wood preserving chemical.

Creosote is a complex mixture containing more than 250 individual compounds. On average, it consists of 85% polynuclear aromatic hydrocarbons (PAHs), 10% phenolic compounds, and 5% nitrogen-, sulfur-, and oxygen-heterocyclic compounds. The components of creosote such as PAHs have very low solubilities, and sorb strongly to geologic media. As a result, creosote DNAPL-contaminated sites seldom create large dissolved contaminant plumes in ground water (Feenstra and Cherry, 1996). In addition, creosote has physical and chemical properties which makes it the least mobile of the common dense ("heavy") liquid contaminants (Figure 10). Its specific gravity ranges between 1.01 and 1.20 (specific gravity of water is 1.00) and its typical viscosity of 10 to 70 centipoise (cP) is much higher than water (1 cP).

Free-phase DNAPL creosote and its dissolved derivatives are found at the site. Site-specific dissolved chemicals include various phenolics, PAHs and single-ring aromatics.

Extent of ground-water contamination at the SWP site was defined with 35 monitoring wells in soil and 58 monitoring wells in rock, placed at specific locations selected after identifying potential sources of DNAPL and directions of ground-water flow (SWP, 1991). The horizontal extent of ground-water contamination associated with past operations at the plant is defined for both the residual soil and fractured rock immediately underlying the site (SWP, 1991). The dissolved-phase contamination in the fractured rock (top of the Stones River Group) extends in the direction of ground-water flow from the plant area toward Chattanooga Creek and is contained within the SWP property boundaries in its entirety (SWP, 1991).

The vertical extent of dissolved constituents in ground water beneath the site is limited by the presence of the low hydraulic conductivity rock zone as shown in Figure 4. Heavy creosote has moved downward into the subsurface soil and rock from points of release to depths where low hydraulic conductivity rock exists, as previously described in the *Hydrogeology* Section. Common behavior of heavy liquids in situations similar to the SWP site is shown in Figure 5 (modified from Pankow and Cherry, 1996). DNAPL first forms pools of limited extent at the boundary between the residual soil and the rock beneath the points of release. It then moves downward into the rock through fractures and into "voids" until it reaches low-hydraulic conductivity rock (Figures 4 and 5). Investigative drilling at the SWP site shows that, when found below the points of release, creosote commonly accumulates at top of rock and in fractures in the rock. Creosote has been shown to penetrate only into the infrequent fractures in the low hydraulic conductivity rock (SWP, 1990).

Therefore, the vertical extent of DNAPL at the site is interpreted not to extend a significant depth into the low hydraulic conductivity rock. Where present in the low hydraulic conductivity rock, DNAPL is within the less frequent, near-vertical fractures. Considering that there is no continuing release of creosote at the site (SWP terminated all its operations in 1988), and that monitoring wells where DNAPL was discovered do not show significant change in accumulations, it is likely that the vertical extent of creosote has reached a steady state condition, and is not expected to increase significantly in the future.

5.0 MIGRATION OF DNAPL AND DISSOLVED CHEMICALS IN ROCK AQUIFER

Migration of free-phase creosote and its dissolved derivatives in rock at the SWP site occurs in two ways:

- heavy creosote (DNAPL) migrates primarily due to gravity forces in a mostly vertical direction through fractures and other rock discontinuities of sufficient size, and
- dissolved constituents are transported through fractures/discontinuities in the same general direction as ground-water flow (see Figure 5).

In naturally-occurring fracture systems, variations in fracture width and length will have a major influence on DNAPL movement. It has been shown that in rocks where there is a significant spatial variation in the fracture dimensions for individual fractures, the ground-water flow and dissolved-phase flow do not occur uniformly across fractures. Therefore, it is generally not possible to characterize a real fracture system in sufficient detail to allow precise quantitative predictions (modeling) of dissolved constituents behavior within a fractured medium (Johnson and Kueper, 1996). However, from the past experience at many sites contaminated with DNAPLs it is possible to assess the potential for DNAPL movement at a specific site. Figures 10 through 13 illustrate elements and principles, as related to the SWP site, that are commonly used to predict fate and transport of free-phase heavy liquids, such as creosote, and dissolved chemicals in ground water.

Two main factors affect travel and resident time of contaminants in the rock aquifer at the SWP site. These factors are:

- mobility of free-phase creosote (see Figure 10)
- hydraulic conductivity of the rock aquifer (Figure 11).

As mentioned earlier, creosote has physical and chemical properties which makes it the least mobile of the common dense ("heavy") liquid contaminants. At the same time, the hydraulic conductivity of the rock aquifer (i.e., the amount of interconnected fractures) at the SWP site decreases with depth as determined by hydraulic testing of boreholes and monitoring wells. Combined, these two factors limit lateral and vertical movement of free-phase creosote at the

SWP site. Figure 12 shows travel time and distance of free-phase creosote for various hydraulic conductivities of the rock aquifer at the SWP site adjusted for the creosote's density and viscosity. For example, the maximum theoretical horizontal distance traveled in 100 years is 30 feet for rock with relatively high hydraulic conductivity (fractured rock immediately underlying the residual soil with $K=1x10^{-4}$ cm/sec). However, the actual direction of movement of heavy creosote is not horizontal, but vertical or near vertical since it travels mainly due to the force of gravity as illustrated in Figure 13. This means that the actual horizontal distance of creosote travel would be much smaller than 30 feet in the more permeable fractured rock. This distance decreases even further for the less permeable rock present at depths of 60 or more feet below land surface where the hydraulic conductivity of the rock aquifer is less than $1x10^{-7}$ cm/sec. For example, at these depths creosote will move less than 3 feet in 10,000 years. In addition, as it continues to move downwards into the rock, creosote detected in isolated pools at the contact between the residual soil and the fractured rock will also practically stop moving once it reaches depths greater than 60 feet below land surface. This means that the detected free-phase creosote at the SWP site, both in the more permeable (i.e., severely weathered and fractured) and less permeable (i.e., less fractured and only slightly weathered along fractures) portions of the rock aquifer, will be naturally contained within the site boundaries and not pose a threat for any of the area's aquifers and ground-water supply sources.

Dissolved constituents emanating from free-phase creosote at the site travel with ground water but at lower velocities due to various natural attenuation processes such as dispersion, diffusion, sorption, chemical degradation, and bacterial activity. As shown in Figures 4 through 7, ground-water flow (and the flow of dissolved constituents) in the rock aquifer underlying the SWP site is naturally toward Chattanooga Creek. The interception trench, parallel to Chattanooga Creek, was installed by SWP to intercept potential migration of dissolved constituents in the rock aquifer. No dissolved creosote constituents have been detected in the Chattanooga Creek water, either before or after installation of the interceptor trench.

6.0 CONCLUSION

Evidence collected during more than 10 years of investigations and remediation at the SWP site in Chattanooga shows that:

- Eree-phase creosote is heavier and much more viscous than water and moves in a predominantly vertical direction until it reaches less fractured rock characterized as having a low hydraulic conductivity (less than 1×10^{-7} cm/sec).
- Physical characteristics of free-phase creosote and gravity forces prevent its migration off site.
- Detected contamination of rock with free-phase creosote does not extend to a significant depth into the low hydraulic conductivity rock underlying the fractured rock aquifer; it is likely that its vertical extent has reached a steady state condition (i.e., it is not expected to increase in future).
- There is no continuing release of creosote at the site since SWP terminated all its operations in 1988.
- Creosote derivatives dissolved in ground water travel with ground water toward Chattanooga Creek within the site boundaries and are intercepted by ground water extraction (intercept trench) to prevent discharge into the creek.
- None of the water wells and ground-water production aquifers surrounding the SWP site are in the path of ground-water flow carrying dissolved constituents.

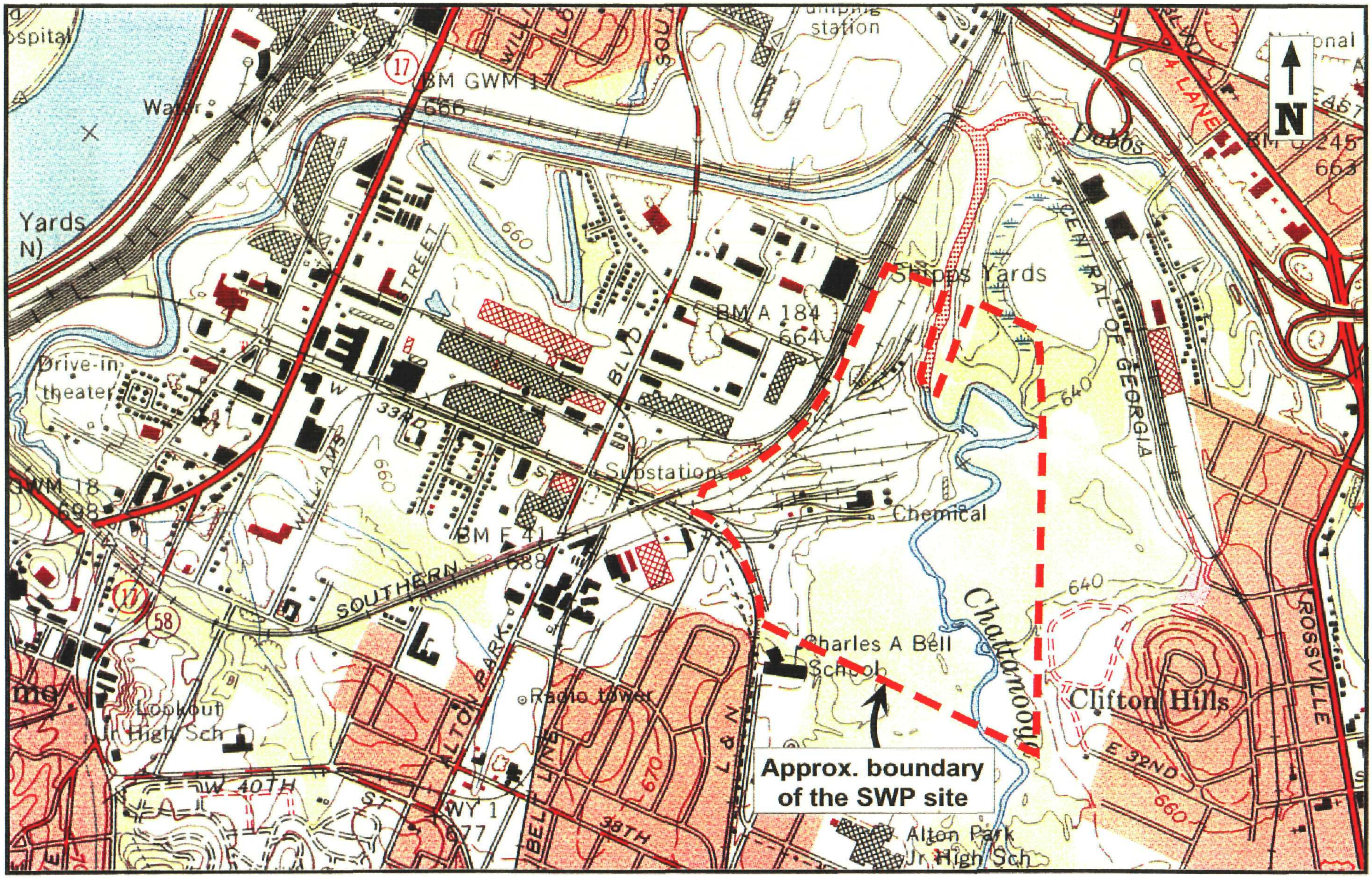
Based on the above mentioned facts, it is our conclusion that there is no risk to human health and the environment associated with free-phase creosote and its dissolved constituents in the rock aquifer underlying the SWP site in Chattanooga, Tennessee.

USDA, 1980. *The biologic and economic assessment of pentachlorophenol, inorganic arsenicals, creosote, Volume I: Wood preservatives.* U.S. Department of Agriculture Technical Bulletin 1658-I, 435 p.

Wilson, R.L., 1979a. *The stratigraphy of exposed rocks in Hamilton County, Tennessee.* In: Geology of Hamilton County, Tennessee, Tennessee Division of Geology, Bulletin 79, p. 15-37.

Wilson, R.L., 1979b. *Ground-water resources of Hamilton County, Tennessee.* In: Geology of Hamilton County, Tennessee, Tennessee Division of Geology, Bulletin 79, p. 117-128.

FIGURES

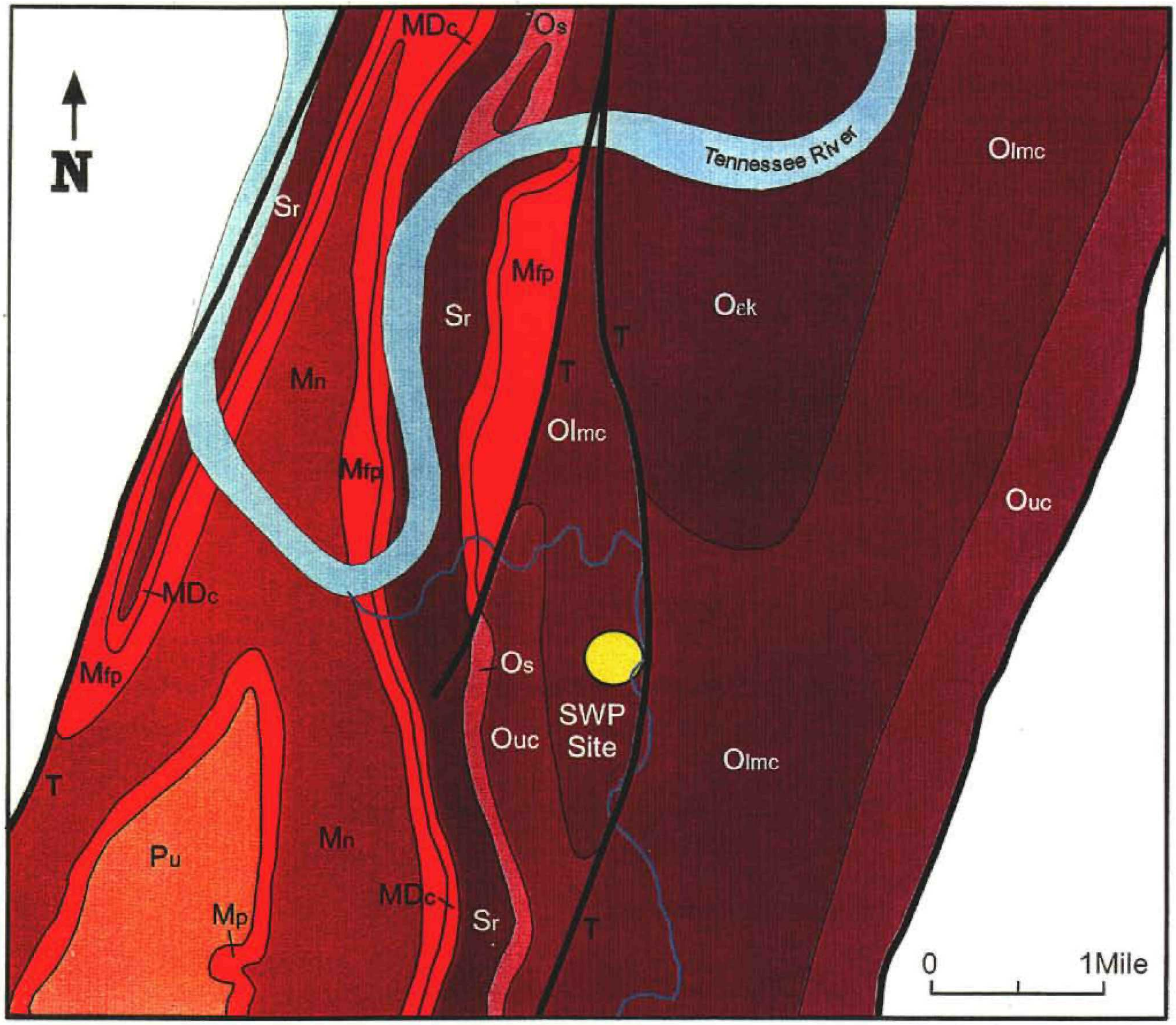


0 0.5 miles

Source: USGS 7.5 MINUTE SERIES TOPOGRAPHIC QUADRANGLE CHATTANOOGA 105-SE

Figure 1 Location of the SWP site in Chattanooga, Tennessee.

Figure 2 SWP performed extensive cleanup and remediation of contaminated soil and groundwater at the site.



Modified from Rodgers, 1953

LEGEND

Pu	Undiffrentiated Pennsylvanian	Os	Sequatchie Formation; siltstone and shale
Mp	Pennigton Formation; mixture of shale, silty dolomite and sandstone	Ouc	Upper Chickamauga; limestone
Mn	Newman Limestone	Olmc	Lower to Middle Chickamauga; limestone with shales and mudstones (Stones River Group underlying the site)
Mfp	Fort Payne Chert	Oєk	Knox Group; dolomite
MDc	Chattanooga Shale	(line)	Thrust Fault
Sr	Rockwood Formation; sandstone, and shale with beds of limestone	T	Upthrown Side

Figure 3 Regional geology of the SWP Chattanooga site.

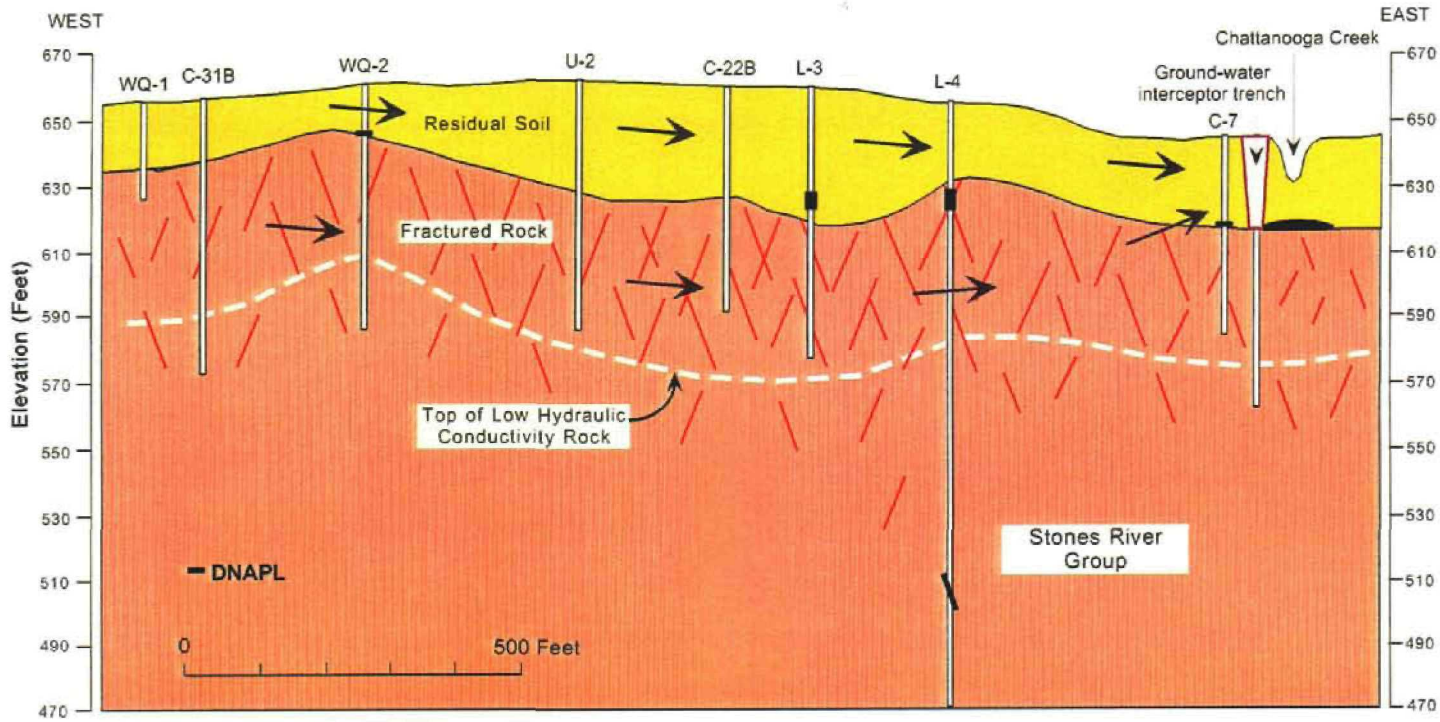


Figure 4 Geologic cross-section (West-East) through the SWP site (SWP, 1988, updated). Direction of groundwater flow in both the soil and the rock is shown with arrows.

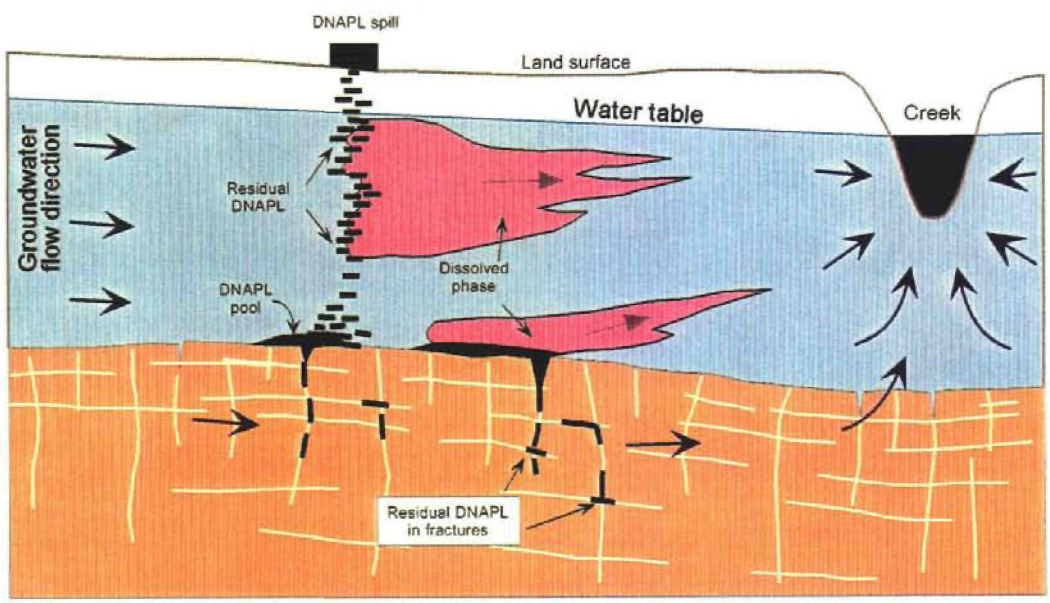


Figure 5 Migration of DNAPL (creosote) and dissolved phase in saturated soil and rock as applied to the SWP site (modified from Pankow and Cherry, 1996).

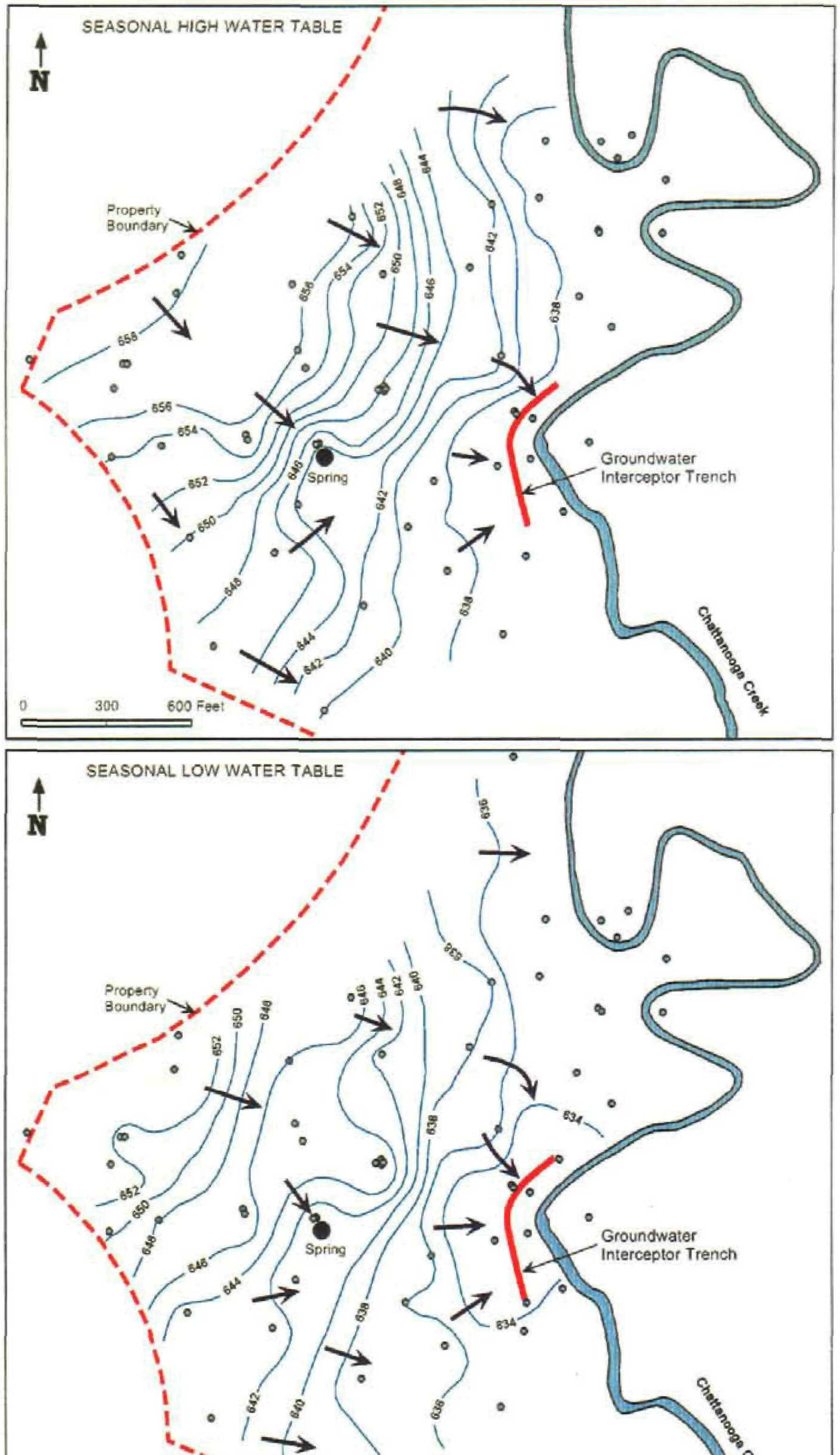
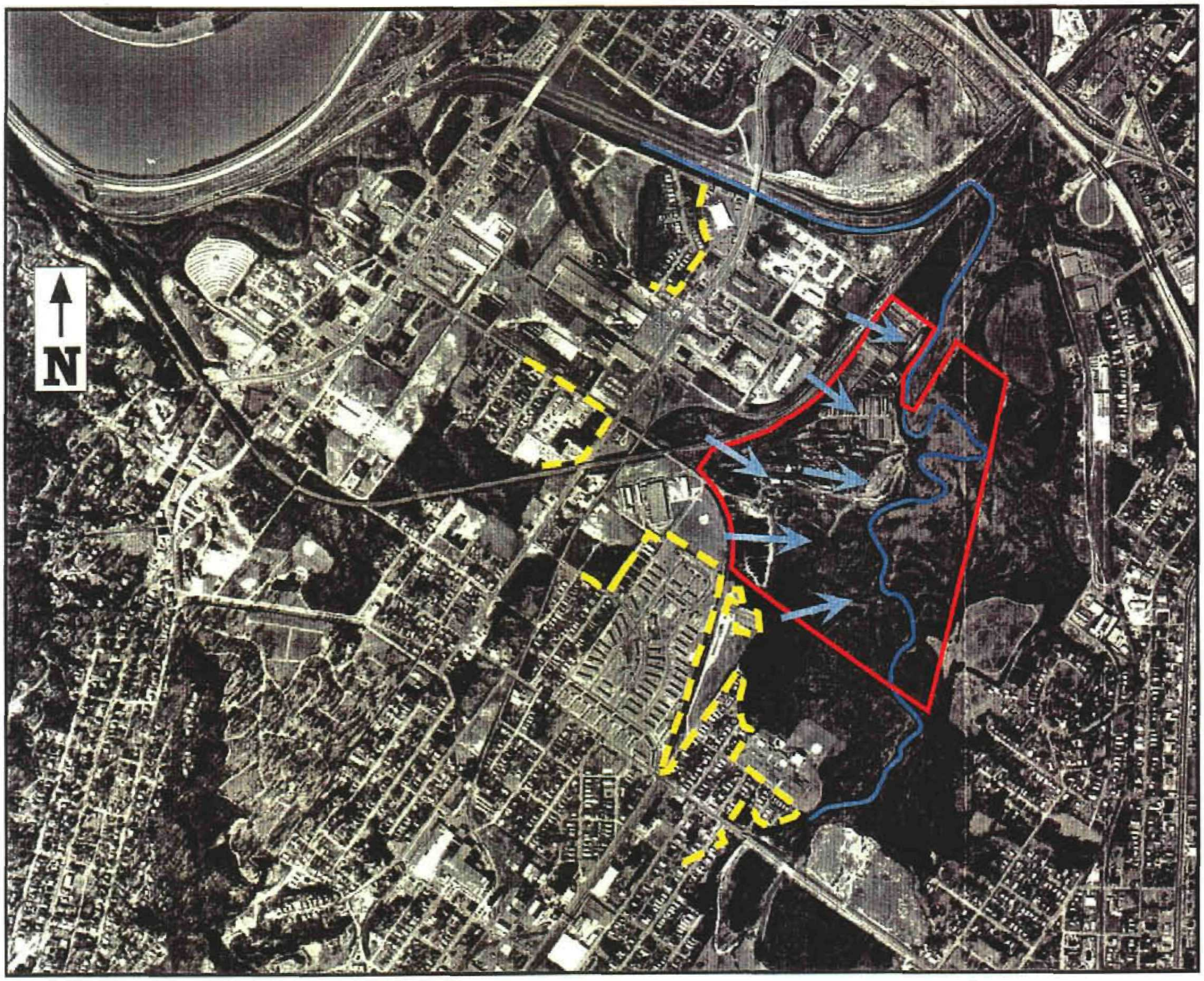


Figure 6 Contours of groundwater elevation (in feet) in rock aquifer and directions of groundwater flow (shown with arrows). Circles denote monitoring wells.



Legend

Approximate boundary of the site

Boundary of nearby residential areas

Direction of groundwater flow in rock

Chattanooga Creek

Figure 7 Aerial photograph of the vicinity of the SWP site, Chattanooga, Tennessee. All groundwater flow in rock at the site is away from nearby residential and industrial areas, and is directed toward Chattanooga Creek.

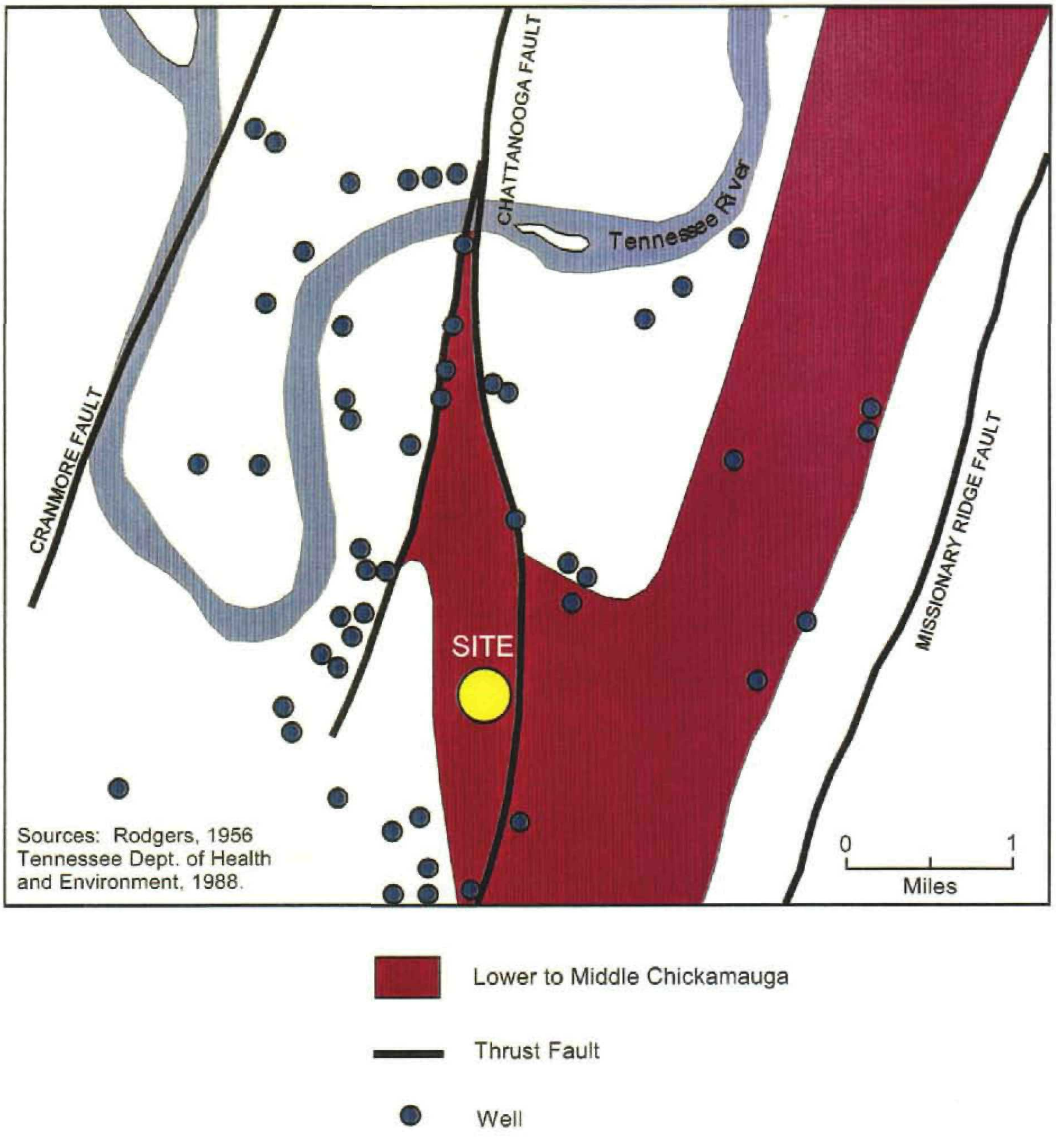


Figure 8 Wells surrounding the SWP site area (SWP, 1988).

Figure 9 SWP constructed an extensive drainage system for controlling surface water runoff at the site. Together with impermeable covers over former ponds and the natural clay soil percent at the site, this surface-water drainage system minimizes infiltration of surface water into soil and the potential for movement of the contaminants off site.

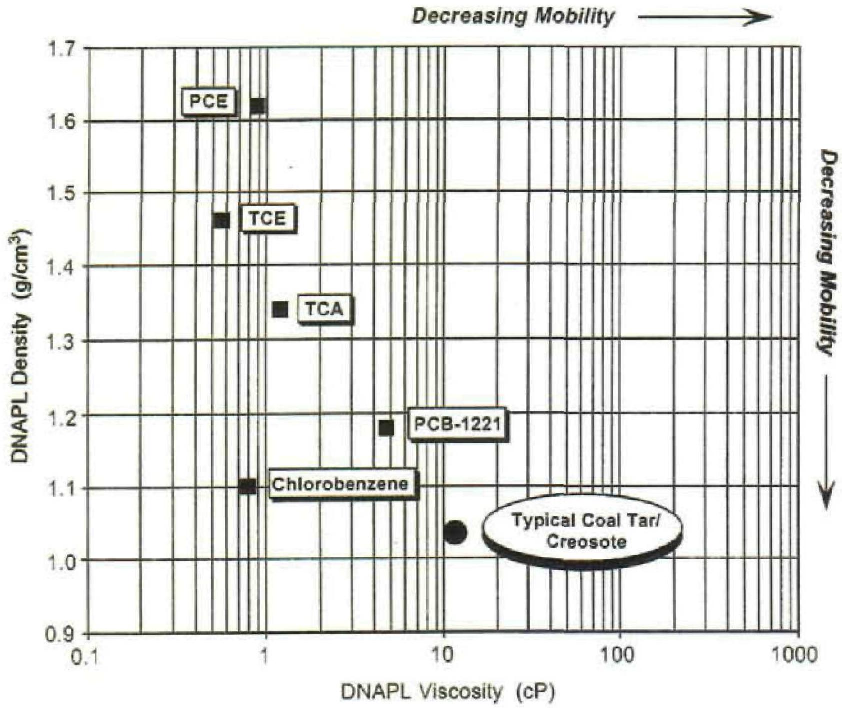


Figure 10 Relative mobility of common DNAPL chemicals presented by the DNAPL density and viscosity (modified from Pankow and Cherry, 1996).

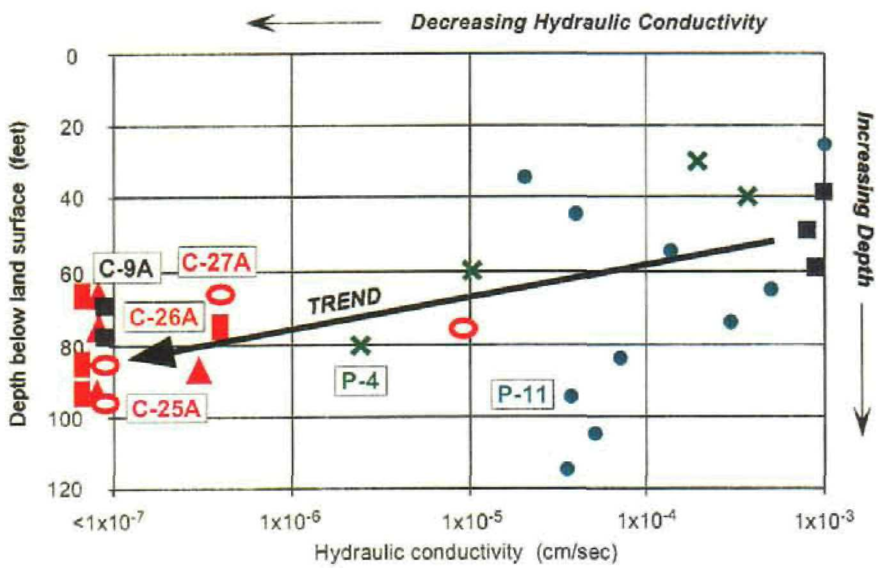


Figure 11 Decrease of hydraulic conductivity in the rock as determined with packer tests in the individual wells.

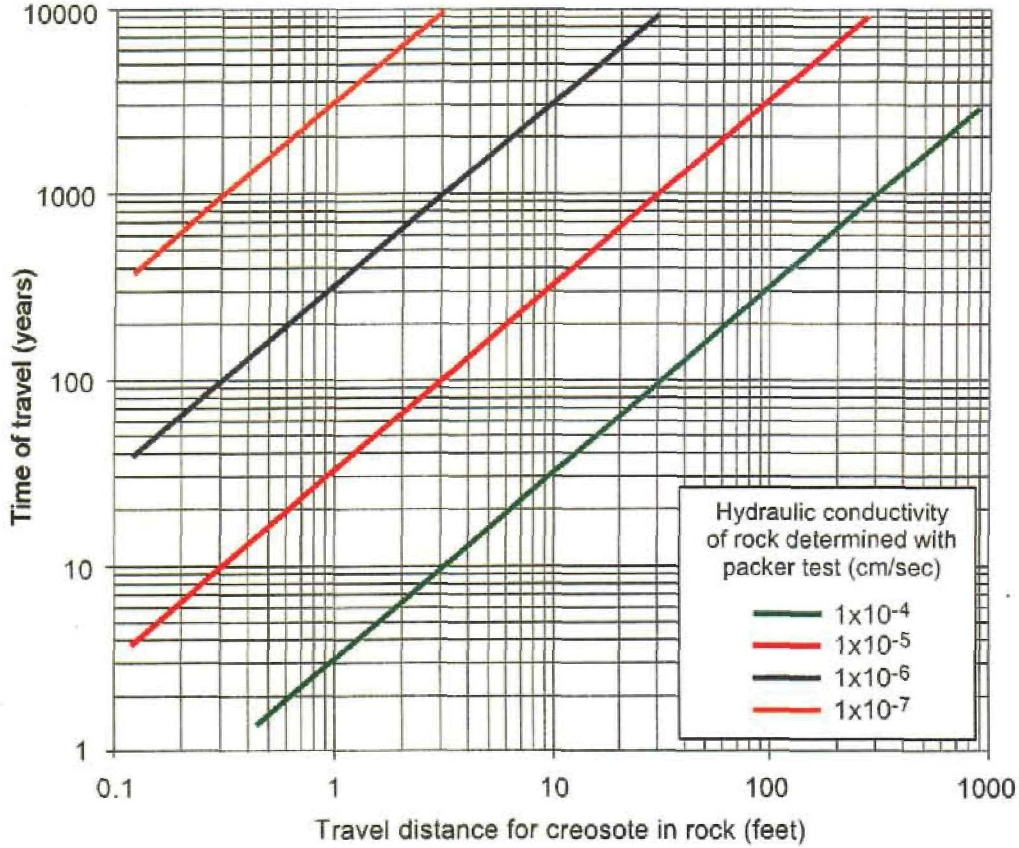


Figure 12 Time versus travel distance of creosote in rock based on packer test data from monitoring wells at the SWP site.

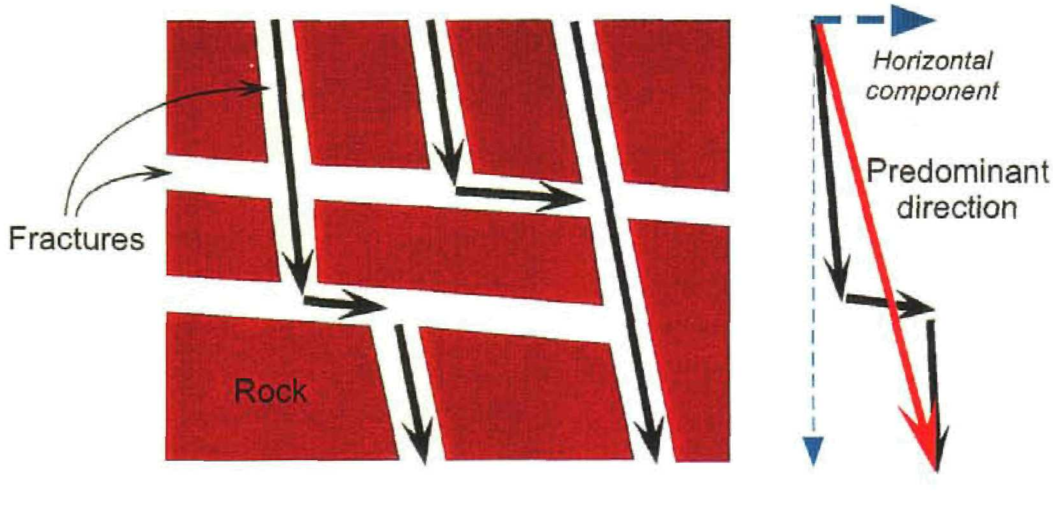


Figure 13 Schematic presentation of the movement of creosote (DNAPL) in fractured rock under the influence of gravity. Predominant direction traveled (red line on right) is mostly vertical due to fractures in the rock and the heavy creosote.

Figure 14 SWP regularly monitors movement of groundwater and dissolved constituents in groundwater with an extensive network of monitoring wells. Contaminated groundwater in soil and rock is being intercepted by pumping from trenches (bottom photograph).